

QUANTITATIVE ANALYSIS OF COALS AND COAL DERIVATIVES BY
CP/MAS- ^{13}C -NMR SPECTROSCOPY

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This paper reports experiments which are designed to ascertain the degree to which the CP/MAS- ^{13}C -nmr technique can be used in a quantitative sense in analysis of coal and coal derivatives. The quantitative capability of the experiment as applied to diamagnetic organic molecules is well documented (1). The uncertainty in the analysis of coals arises from the presence of a substantial organic-based free-electron spin density and from the uncertainty in the hydrogen distribution in these typically low H/C materials. The possibility exists that a fraction of the carbon in a coal experiences electron-nuclear interactions which render the signal invisible, broadened and/or paramagnetically shifted, or is in an environment depleted of hydrogen and unable to yield a ^1H - ^{13}C CP signal.

To what extent are the carbons in coal detected with unit intensity response? The experiment selected to address this question entails introducing into the coal a known quantity of carbon designed to yield unit intensity response under the analysis conditions. The experimentally measured area ratio representing introduced carbon/native coal carbon from the CP/MAS- ^{13}C -spectrum is then compared with the same ratio determined in an unambiguous, independent experiment.

Chemical Modification of ILL. #6-Vitrain

The introduced carbon is incorporated by methylation of the heteroatoms of the coal which undergo base-catalyzed alkylation. In ILL. #6 vitrain these sites are predominantly (80-85%) phenolic residues. The balance of the introduced methyl groups are bonded to other functional groups. There is clear chemical shift evidence for methyl ester and aminomethyl groups and perhaps a small amount of sulfhydryl or select carbon methylation.

The methylation is performed with ^{14}C , ^{13}C -double-labelled methyl iodide. The measure of introduced carbon is obtained by ^{14}C -radioassay techniques, which, together with elemental analysis of the coal derivative, provides the benchmark ratio needed to evaluate the nmr integrations.

Large errors in the ^{14}C and ^{13}C ratio determinations can occur if solvents and/or reagents used in the derivitization contaminate the product. The extent of such unwanted incorporation in the present experiments have been measured by using ^{14}C -labeled solvents and reagents in parallel experiments.

Initial methylations were performed using tetra-*n*-butyl ammonium hydroxide in aqueous THF following literature procedures (2). Repeated attempts to remove $(\text{nBu})_4\text{N}^+\text{X}^-$ salts from the product using published methods were unsuccessful in our hands. The reagent can be removed by methanol washing, but a significant fraction of the coal is also solubilized by this solvent.

To prepare an O- CH_3 coal derivative free of carbon-containing reagents, a procedure for alkylation of coal using KOH in aqueous THF was developed. The methylation of ILL. #6 vitrain using this system introduced 4.6 methyl groups/100 coal carbons after 5 days reaction, ca. 10% fewer than obtained with the tetra-*n*-butylammonium

hydroxide/aqueous THF system. For the present purpose, complete alkylation is not required; the product, Ill. #6-OCH₃, obtained following a single methylation step is analyzed in Table 1. Another product listed in Table 1, Ill. #6-XCH₃, has been prepared by stirring Ill. #6 vitrain and methyl iodide (91.2% ¹³C-enriched, 3-fold molar excess based on five acidic sites/100 coal carbons) in THF for five days. Under these conditions little aromatic methylether formed. The incorporation of methyl groups occurs predominantly on acid and amine functional groups.

THF retention in the coal products is minimal (<0.8 wt%) in all alkylation procedures.

CP/MAS-¹³C-NMR Analysis

The aromatic carbon fraction of coals, f_a , derived from CP/MAS-¹³C-nmr measurements are generally determined from aromatic and aliphatic carbon resonance area measurements taken from a single spectrum recorded under optimum or near optimum signal-to-noise conditions (cross polarization contact time = 1 ms). Reported f_a values determined in this fashion assume that the conditions for quantitative signal intensity response in this experiment, namely

$$T_{CH} \ll t_{cp} \ll T_{1\rho H}$$

are applicable. T_{CH} is the ¹H-¹³C cross polarization time constant under the Hartmann-Hahn condition, t_{cp} is the experimental cross polarization contact time, and $T_{1\rho H}$ is the proton spin-lattice relaxation time in the rotating frame. Single spectrum analysis of f_a requires that a homogeneous $T_{1\rho H}$ characterize the entire sample.

It has been shown that the aromatic and aliphatic resonance envelopes of coals generally display nearly homogeneous but different $T_{1\rho H}$ behavior (3). The ratio $T_{1\rho H}$ (aromatic)/ $T_{1\rho H}$ (aliphatic), with typical values of 0.8-1.2 for Ill. #6 vitrain derivatives, can be altered by chemical modification.

While the inequality $T_{CH} \ll t_{cp} = 1$ ms is valid for protonated carbon sites in coals, it is only marginally met for the non-protonated aromatic carbon fraction of Ill. #6, which reveals an average T_{CH} of 350 ± 100 μ s. This value should not differ significantly for other bituminous coals.

These considerations indicate that it is worthwhile to evaluate CP/MAS-¹³C-nmr data of coals more critically to assess the errors which may be introduced by single spectrum analysis.

The general expression given by Mehring (4) which describes the development of carbon signal intensity in the spin-lock, CP/MAS-¹³C-nmr experiment with non-negligible $T_{1\rho H}$ relaxation is

$$A(t) = KN \frac{T_{1\rho H}}{T_{1\rho H} - T_{CH}} (e^{-t/T_{1\rho H}} - e^{-t/T_{CH}}) \quad 1)$$

where $A(t)$ is ¹³C signal intensity at $t = t_{cp}$, N represents the number of acquisitions and K is a constant proportional to the number of ¹³C spins and spectrometer sensitivity. By restricting the cross polarization contact time to values for which $t_{cp} \gg T_{CH}$ and $e^{-t_{cp}/T_{CH}} \ll e^{-t_{cp}/T_{1\rho H}}$, Equation 1 reduces to

$$A(t) = KN \frac{T_{1\rho H}}{T_{1\rho H} - T_{CH}} (e^{-t/T_{1\rho H}}) \quad 2)$$

Examination of typical $T_{1\rho H}$ and T_{CH} values for the coal derivatives under consideration shows that the use of cross polarization times > 2 ms satisfy the restrictions which lead to Equation 2. To evaluate f_a the spectrum is recorded at five contact times > 2 ms and the separate aromatic and aliphatic resonance areas are non-linear least-squares fit to Equation 2. K is evaluated at $t_{cp} = 0$ as

$$K = A_0 \frac{T_{1\rho H} - T_{CH}}{T_{1\rho H}} \quad 3)$$

and f_a is given by $K(\text{arom})/[K(\text{arom}) + K(\text{aliph})]$.

The application of Equation 3 requires estimates of T_{CH} for several carbon types in coals. Previous studies of coals indicate that T_{CH} values of 35, 65 and 350 μ s for protonated carbons (aromatic and aliphatic), methyl carbons (methylether) and non-protonated aromatic carbons, respectively are acceptable estimates for the present analysis. The aliphatic resonance band is considered to have a negligible fraction of non-protonated carbons and 60% of the aromatic resonance band is considered to be non-protonated carbon (5).

Table 1 summarizes the aromaticity values for Ill. #6 vitrain calculated using Equation 3. Intensity data over the range of contact times 1.0-8.0 ms yields f_a of $.660 \pm .003$. The same data set, minus the intensity data for the 1 ms t_{cp} , yields a calculated f_a of $.707 \pm .006$. The 1 ms data strongly influences the calculation. Equation 3 is not an appropriate expression for analysis of the 1.0 - 8.0 ms data set since the inequality $e^{-t_{cp}/T_{CH}} \ll t_{cp}/T_{CH}$ is not met for 1 ms data. Equation 1 should be used to treat this data. Note that the calculated f_a for the data for which $t_{cp} > 2$ ms is in fair agreement with f_a determined from a single spectrum with $t_{cp} = 1.0$ ms.

Table 1. f_a and Introduced CH₃/100 Coal Carbons for Ill. #6 and Derivatives.

	f_a	Introduced CH ₃ /100 Coal Carbons	
	Ill. #6	Ill. #6-OCH ₃	Ill. #6-XCH ₃
1.0-8.0ms t_{cp} range	$0.660 \pm .003$	5.84	0.18
2.0-8.0ms t_{cp} range	$0.707 \pm .006$	5.78	0.1
1.0ms t_{cp} time	$0.697 \pm .02$	5.72	0.21

The number of methyl carbons introduced into the coal matrix is determined by assuming that f_a of Ill. #6 vitrain is valid for the original coal carbon of the products, i.e., interconversion of sp^2 and sp^3 carbons does not occur as a consequence of the derivitization. Hence, f_a of Ill. #6 vitrain and the aromatic resonance area of the product allow partitioning of the aliphatic resonance area into components representing native coal carbon and introduced carbon. This analysis is summarized in Table 1 for the two coal derivatives, Ill. #6-OCH₃ and Ill. #6-XCH₃.

Note that the calculated value for the number of methyl groups introduced into Ill. #6-OCH₃ using the fitting procedure (Equation 3) is independent of the t_{cp} range and f_a assigned to the original coal, as long as the analysis of Ill. #6 vitrain and Ill. #6-OCH₃ is internally consistent. This is simply a statement that to within the error of the fit of the data to a single exponential, no detectable carbon intensity accrues in the spectrum between 1.0 and 2.0 ms. The fitting procedure simply corrects the measured areas for the differences in $T_{1\rho H}$ between the coals and for the differences of $T_{1\rho H}$ between the aromatic and aliphatic resonance bands of each coal.

The calculated values for the number of methyl groups introduced into the coal using single spectrum analysis with $t_{cp} = 1.0, 2.0$ and 3.0 ms, is 5.72, 5.34 and 5.01, respectively, and indicate the magnitude of the error which is introduced by the $T_{1\rho H}$ differentials between the coal and its derivative. Clearly the value at $t_{cp} = 1.0$ ms is indistinguishable from the values obtained by the full fitting procedure. Thus a 1.0 ms cross polarization contact time is a judicious compromise value consistent with a nearly complete cross polarization signal from all carbons including detectable non-protonated carbons and minimum error introduced by differential $T_{1\rho H}$ relaxation effects.

The methyl incorporation values shown in Table 1 for Ill. #6-XCH₃ show the same behavior but have larger relative error, a result of the small area changes in the product relative to Ill. #6 vitrain.

Comparison of ¹³C-NMR and ¹⁴C-Radioassay Analysis

The number of methyl groups found in Ill. #6-OCH₃ and Ill. #6-XCH₃ by the radioassay technique is 4.64/100 coal carbons and 0.20/100 coal carbons, respectively. The error in these values is largely determined by the error in elemental analyses and is <2%. The values determined by nmr analysis (1.0 ms CT) are $5.72 \pm 1.1/100$ and $0.21 \pm 0.04/100$ coal carbons, respectively. The 20% error associated with the nmr values is derived for the use of single spectrum analysis and is the worst case error calculated by allowing f_a of Ill. #6 vitrain and Ill. #6-OCH₃ to vary $\pm .02$ from their measured values. We conclude that, within the estimated error of the nmr measurement, the CP/MAS-¹³C-nmr method does accurately monitor total carbon signal in the examined coals.

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